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Synthesis and Characterization of A New Cadmium Complex, Cadmium [(1,10-phenanthroline)(8-hydroxyquinoline)]Cd(Phen)q

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Abstract

A new photoluminescence material cadmium [(1,10-phenanthroline)(8-hydroxyquinoline)] Cd(Phen)q has been synthesized and characterized.The prepared material Cd(Phen)q was characterized by Fourier-infrared spectroscopy(FTIR),Nuclear magnetic resonance spectroscopy (NMR),Thermo gravimetric analysis (TGA), UV-visible spectroscopy and photoluminescence (PL). Solution of this material Cd(Phen)q in toluene showed absorption maxima at 256nm and 295nm which may be attributed to the moderate energy ($\pi - \pi^*$) transitions of the aromatic rings while absorption maxima at 335nm and 387 nm observed were due to the coordination of cadmium and organic ligands (Phen and q).The photoluminescence spectrum of Cd(Phen)q in toluene solution showed peak at 510nm.This material is thermally stable up to 400^0C. The time resolved photoluminescence spectra of this material Cd(Phen)q showed two life time components, 3.8 ns and 15 ns respectively.

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Keywords: Cadmium complex Cd(Phen)q, Luminescence,Theramal stability

1. Introduction

In organic light emitting diodes (OLEDs),green light emitters have attracted much attention due to their stability and brightness as reported by Xiang et al. (2013) and jwo et al (2013).The need for stable and efficient light

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emitting molecules become obvious due to the growing market of organic light-emitting diodes which are meanwhile used in low-cost displays.OLEDs with low molecular weight molecules are promising candidates for lighting applications and large-area displays due to their low power consumption, high wide viewing angle and ease of fabrication as reported by Tang and Van Slyke (1985) and Baldo et al. (1998) . A lot of research is going on to make new small molecule, photo luminescent materials due to their potential application in flat panel displays based on organic light emitting devices(OLEDs).Small molecule, photo luminescent materials with low molecular weight have been used in OLEDs.These small molecules had been synthesized by many groups by taking different metals like aluminum(Al),zinc(Zn),iridium(Ir),gadolinium(Gd),europium(Eu), platinum (Pt) etc. with taking different ligands like 2-(2-hydroxyphenyl) benzoxazole (HPB) 8-hydroxyquinoline(q),1,10 phenanthroline(Phen), 2,2'bipyridine(Bpy) etc. as reported by Yang et al.(2005), Rai et al.(2008), Tao et al. (2013), Tang et al. (2014), Reyes et al. (2013),Sano et al.(1995) and Sotomaya et al. (2005). These electroluminescent materials emit light in the visible region. Nowadays cadmium complexes also have been synthesized by different groups for their use in OLEDs due to their thermal stability and wide spectral range as reported by Sotoyama et al. (2008),Gao et al. (2014)and Kumar et al.(2010,2011and 2014). In this work, we report the synthesis of a new photoluminescent material cadmium[(1,10-phenanthroline)(8-hydroxyquinoline)] and its optical properties (photoluminescence,UV-visible-spectra), structural properties (FTIR,NMR) and thermal stability (TGA).

2. Experimental details

The synthesis process of cadmium [(1,10-phenanthroline)(8-hydroxyquinoline)] Cd(Phen)q is shown in figure1. The material was obtained by the reaction of the two ligands,Phenanthroline (Phen) and 8-hydroxy quinoline(q) with cadmium acetate (metal ligand) at 1:1:1 molar ratio in ethyl alcohol. A solution of phenanthroline 0.18 g (0.001 mol) (Sigma Aldrich Chemicals) was prepared in 20 ml absolute ethanol (S.D. Fine Chem Limited India) in a 100 ml three neck flask and stirred in nitrogen atmosphere for 30 min and then a solution of 8-hydroxy quinoline 0.145 g (0.001 mol) (Merck, India) in 20 ml of absolute ethanol was added to the reaction mixture, and stirred at 90 °C for 2 h. This was allowed to cool to 70 °C and a solution of cadmium acetate 0.267 g (0.001mol) in 3 ml of deionized water was added drop wise to the reaction mixture. After 2 h of stirring a yellowish precipitate of the complex was separated from the reaction mixture which was filtered and dried at 90 °C in vacuum oven for 24 h.

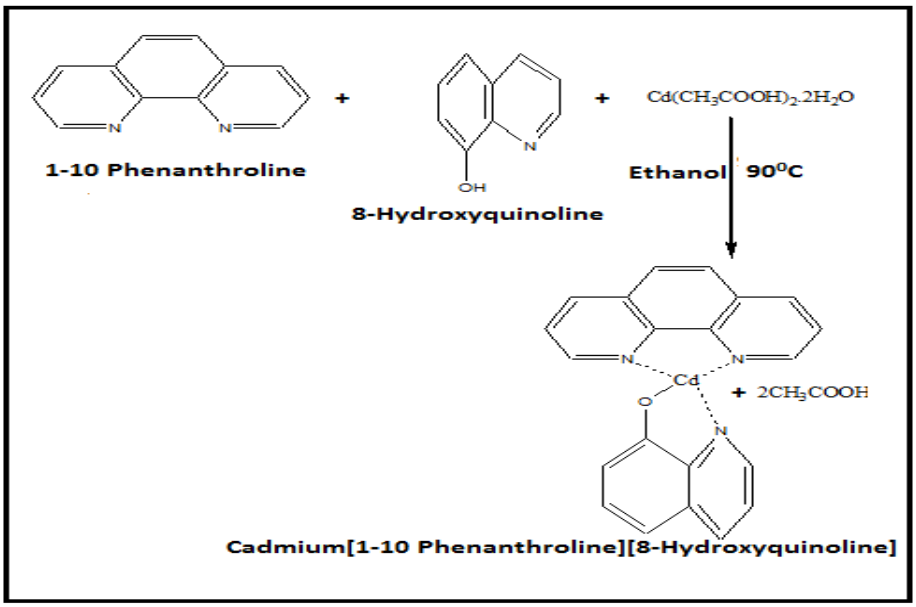

Figure1: Synthesis of Cadmium [(1,10-phenanthroline)(8-hydroxyquinoline)]Cd(Phen)q

3. Result and discussions

3. 1 Structural and thermal characterization of material Cadmium [(1,10-phenanthroline)(8-hydroxyquinoline)]Cd(Phen)q

Characterization of the material was carried out by spectroscopic techniques, Fourier transformation infrared spectroscopy (FTIR), Nuclear magnetic resonance (NMR) and thermal gravimetric analysis (TGA).FTIR analysis of the material as done with a KBr pellet using a Nicolet 5700 spectrometer is shown in figure2. The absorption bands at high wave number (3600-1700 cm^{-1}) were due to localized hydrogen stretching vibrations. The absorption in mid wave number region (1700-1000 cm^{-1}) corresponds to heavy atom (Cd) in-plane and bending vibrations. In the low wave number region below 1000cm^{-1} absorption is attributed to out-of-plane modes. The bands at 1600 and 1577 cm^{-1} are assigned to C=C stretching vibration from the quinoline ligand.The bands observed at 1500 and 1469 cm^{-1} correspond to C=C/C=N stretching associated with both the pyridyl and phenyl group in Cd(phen)q.The vibrations at 1391 and 1325 cm^{-1} are due to C=C/C=N stretching in the quinoline fragments of Cd(phen)q. Pouchert (1983) have suggested that band at 1100cm^{-1} is due to C-O stretching vibration at the C-O-M site. The spectrum they measured showed a sharp absorption band near 1110 cm^{-1} as reported by Pouchert (1983) .In the region below 1000cm^{-1} out-of-plane vibration are usually observed. The most intense out- of- plane absorption in this region was found at 743 cm^{-1}. Cadmium ions form a stable complex with quinoline and phenanthroline via Cd-N bond which is confirmed from absorption observed at 490 cm^{-1}.NMR of the material was done using Mercury Plus 300MHz NMR spectrometer as shown in fig3. We carried out 1D NMR and mass spectrometry studies on complex to deduce its molecular structure. The comparison of ^{1}H NMR spectra of 1,10-phenanthroline, 8-hydroxyquinoline and its corresponding cadmium complex presented in figure 3. Due to presence of unpaired electron spin in Cadmium (I) complex the 1H NMR of complex broadened because of paramagnetic effect (pseudocontact shift) as reported by Karl et al.(1970).The proton assignments were made on the basis of the resonance position and integrated intensity data. Figure 3 revealed that protons of 1,10-phenanthroline in cadmium complex experienced downfield shifts because of the coordination of lone pair electron of 1,10 nitrogen atoms of phenanthroline ligand to cadmium metal and appeared at a different region as compared to its corresponding free base ligand as reported by Matthias et al.(2011) and Georgi and Maria (2003) . For example 2,9, 4,7, 5,6, and 3,8 protons shifted from (8.95- 8.94), (8.20-8.17), 7.63 and 7.58 to (9.17), (8.44), 7.93, and 7.84 ppm. Similarly 8-hydroxyquinoline protons also experienced slight up field or downfield shifts because of coordination to cadmium metal. In mass spectrum fragments M/Z = 293, 438 and 518 are corresponds to [Cd(phen)], [Cd(phen)q] and [Cd(phen)(CH_3CN) K] respectively. In mass spectrum peak at 438 correspond to molecular ion peak which confirmed the formation of Cadmium complex. TGA analysis of the material was done by using SDTA 851Metter-Toledo-star system in the temperature range from 25^0C to 500^0C shown in figure4. This material shows thermal stability up to 420^0C.Initially there was a weight loss at around 100^0C. It may be due to volatile impurity present in the material.

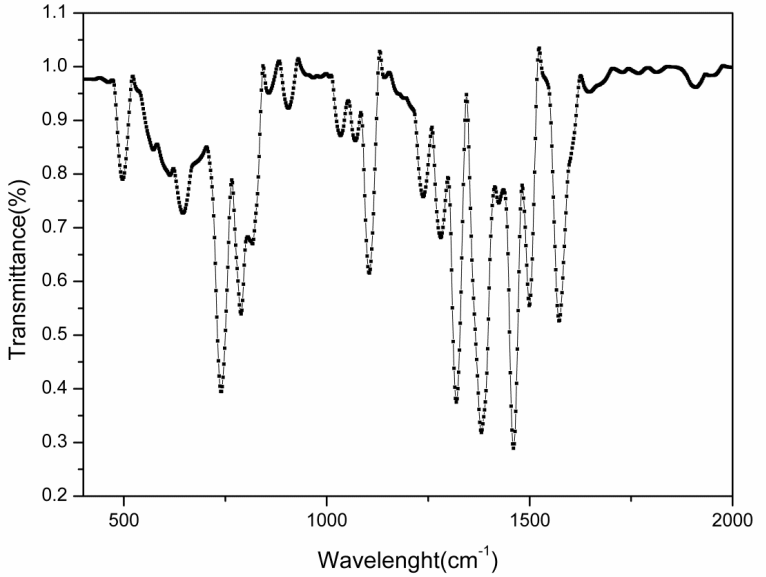

Figure 2:FTIR spectrum of Cadmium [(1,10-phenanthroline)(8-hydroxyquinoline)] Cd(Phen)q

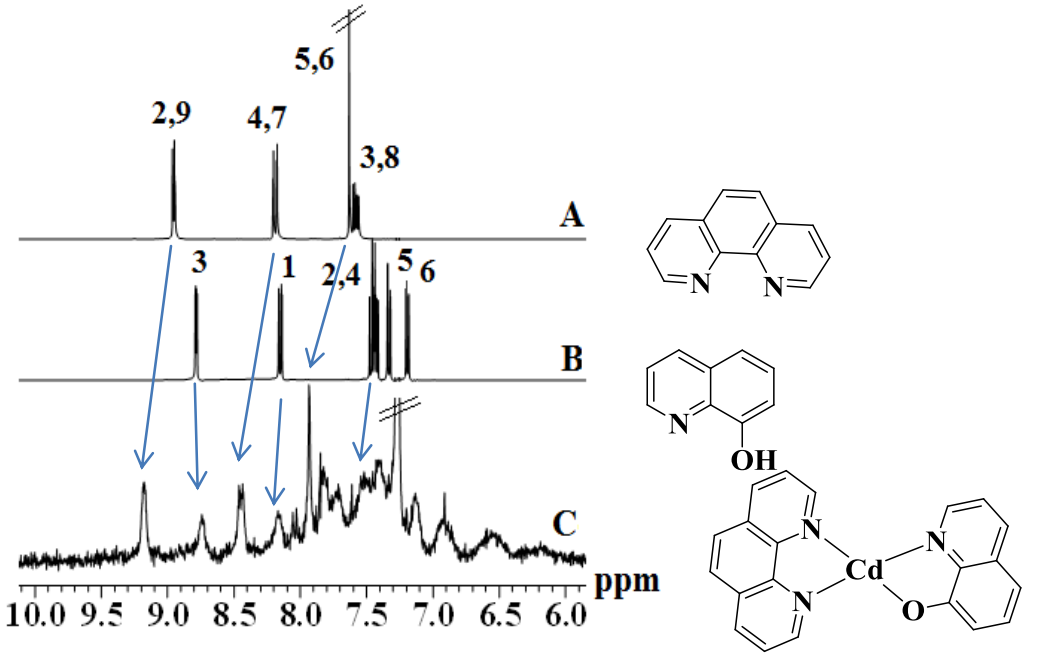

Figure 3. ^{1}H NMR spectrum of 1,10-phenanthroline (A), 8-hydroxyquinoline (B) and Cadmium (I) complex (C) recorded in $CDCl_3$(TMS as standard).

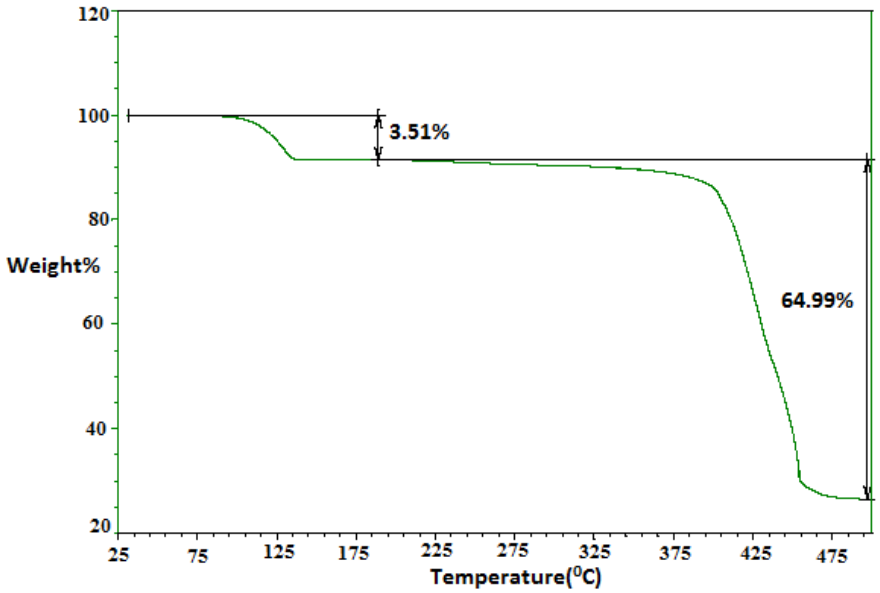

Figure 4: Thermogravimetric analysis of Cadmium [(1,10-phenanthroline)(8-hydroxyquinoline)] Cd(Phen)q

3.2 Optical properties of Cadmium [(1,10-phenanthroline)(8-hydroxyquinoline)] Cd(Phen)q

UV-visible absorption spectra were recorded on a Shimadzu UV-2401 spectrophotometer. The excitation and emission spectra of the material were recorded with a Fluorolog Spectro fluoro meter (Horiba Jobin YVON Fluolog odel FL 3-11) at room temperature. The photoluminescence and UV-visible spectra were obtained in a solution of toluene as shown in figure5. The absorption spectra of this material showed absorption maxima at 256nm and 295nm which may be attributed to the moderate energy ($\pi - \pi^*$) transitions of the aromatic rings while absorption maxima at 335nm and 387 nm observed were due to the coordination of cadmium and organic ligands (Phen and q). Photoluminescence spectra for this material showed the most intense peak at 510 nm.

Time-resolved PL decay spectra were recorded by a time-correlated single-photon counting (TCSPC) system from IBH (UK). During the experiment, the excitation wavelength and repetition rate were 341nm and 1 μHz, respectively. The instrument response time was 800 ps. The time-resolved PL spectrum is given in figure6.The decay curve is fitted by $I = a1e^{-t/\tau 1}+a2e^{-t/\tau 2}$, where τ1 and τ2 are the lifetime of the components with amplitude al and a2 as reported by Zhang et al. (2010). The decay times of the first and second component are 3.8 ns and 15 ns respectively which is well fitted with single exponential functions as reported by Palilis et al. (2005).The bi-exponential behaviour of the decay curve can be explained by a) a fast process which might be attributed to intrinsic decay and energy transfer between host and guest molecules, b) the slow process can be correlated with excitation of host molecules that are further away from the guest molecules and depending on the intermolecular distance between host and guest molecules. However, both the processes contribute to the energy transfer rate which depends on the acceptor concentration as reported by Palilis et al. (2005) .

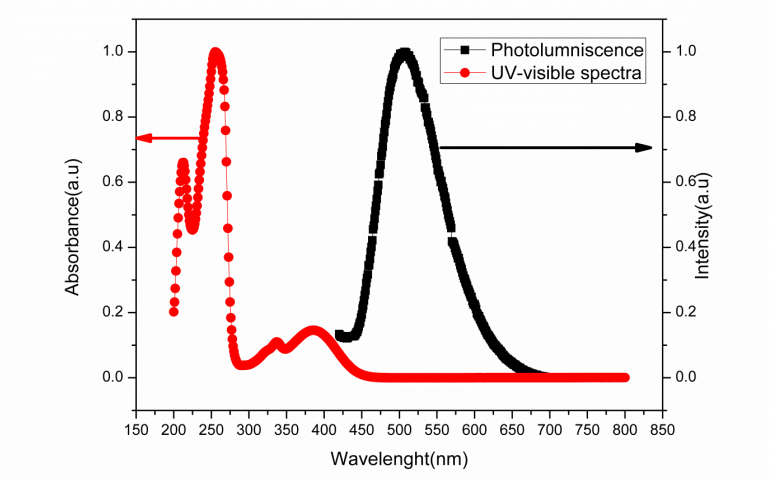

Figure 5: UV-visible and photoluminescence spectrum of Cadmium [(1,10-Phenanthroline)(8-hydroxyquinoline)] Cd(Phen)q

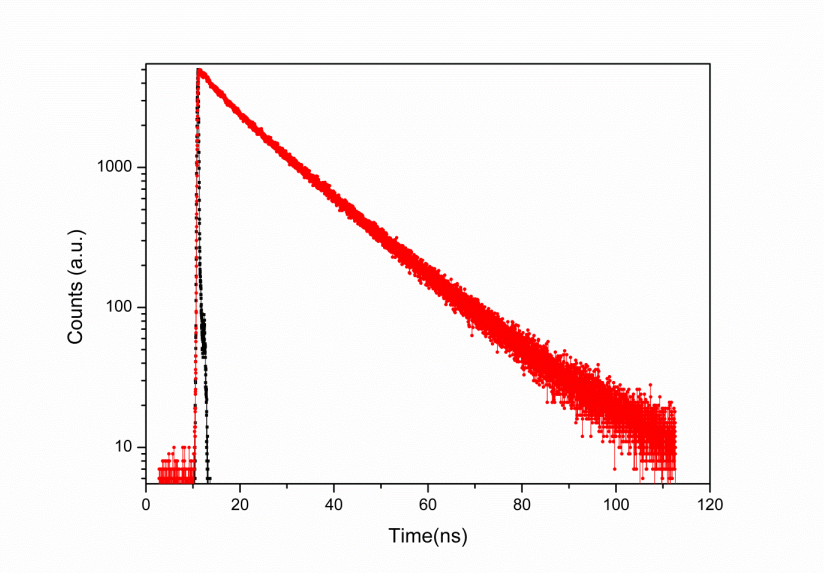

Figure 6: Life time decay of Cadmium [(1,10-phenanthroline)(8-hydroxyquinoline)] Cd(Phen)q

4. Conclusions:

A small molecule, new photoluminescent material cadmium [(1,10-phenanthroline)(8-hydroxyquinoline)] Cd(Phen)q was fabricated with the reaction of (1-10) phenanthroline and 8-hydroxy quinoline(q) ligands with cadmium acetate. This material is stable up to 420^0C **.** The intense peak of photoluminescence of this material shows emission in green region.

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